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(Unexamined Patents Bulletin)

Application Publication No.  
60-12136

Internat. Class.	Qualifier	Internal File No.	Disclosure date: 22 January 1985
B01J 37/02		7624-4G	
35/04		7624-4G	
//B01D53/36		8314-4D	
<hr/> Number of inventions: 1 Request for examination: NO (total 4 pp)			

Title of invention: Coating process and impregnation process for monolithic supports

Patent Application No. 58-121265  
Date of filing: 4 July 1983

Inventor: Noriyuki Tsuge  
c/o Toyota Motor Corp.  
1 Toyota-cho, Toyota, Japan.

Inventor: Shigenori Sakurai  
c/o Toyota Motor Corp.  
1 Toyota-cho, Toyota, Japan.

Inventor: Toshio Funayama  
c/o Toyota Motor Corp.  
1 Toyota-cho, Toyota, Japan.

Applicant: Toyota Motor Corp.  
1 Toyota-cho, Toyota, Japan.

Agent: Masami Hanabusa & Associate, Patent Attorney

**SPECIFICATION**

1. Title of invention

Coating process and impregnation process for monolithic supports

2. Scope of claims

A coating process and impregnation process for monolithic supports characterised as comprising: a step wherein either the peripheral zone of one end of a monolithic support is coated over the desired width and alumina slurry is poured into the cells of the open central zone or a monolithic support the peripheral zone whereof is coated at both ends is immersed in alumina slurry, thereby depositing alumina slurry on the inner walls of the cells of the said central zone, and wherein the monolithic support is then dried and calcined to obtain a monolithic support comprising an alumina coated central zone and a

non-alumina-coated peripheral zone; and a step wherein the said monolithic support clamped between upper and lower rings of the same diameter as the aforesaid central zone is immersed in an aqueous solution of noble metals or the said monolithic support with the peripheral zone of both ends coated is submerged and immersed in an aqueous solution of noble metals, and the support is then dried so that noble metals are impregnated only to the aforesaid central zone.

### 3. Detailed description of invention

#### [Field of industrial utility]

The invention relates to a method of manufacturing monolithic catalysts for cleaning the exhaust gas from internal combustion engines.

#### [Prior art]

Monolithic catalysts have long been used to render innocuous the noxious substances contained in exhausts from internal combustion engines in motor vehicles, etc. A monolithic catalyst is one wherein an integral ceramic structure (the monolithic support) whose interior is provided in honeycomb fashion with numerous through-holes (cells) is coated with alumina whereon noble metals such as platinum, rhodium and palladium comprising the catalytically active moiety are then supported; the noxious substances contained in the exhaust, namely hydrocarbon (HC), carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>), can then be efficiently removed by oxidation or reduction when exhaust gas is passed through the monolithic catalyst. Compared with pellet catalyst, monolithic catalyst also has the advantage of small pressure loss, etc, owing to a high porosity and little formation of fine powder by vibrational attrition.

The converter case that accommodates a monolithic catalyst has ring-shaped peripheral retainers, which are the axial retaining members, at both ends in the direction in which the gas under treatment passes; the exhaust gas channels are therefore closed off where the retainers are located and exhaust gas cannot flow to the cells at the periphery. This means that the available volume of monolithic catalyst is substantially reduced. If, on the other hand, the retainers are eliminated, the catalyst retaining force declines and strength under vibration is reduced; consequently, robust converters become larger as the monolithic catalyst is increased in size to compensate for the part closed off by the retainers, and this creates fresh problems.

Emphasis has therefore been placed on improving the performance of the monolithic catalyst itself, and means of improvement have been proposed such as gradually reducing the loading of noble metal from the central zone of high gas throughput outward to the

peripheral zone; however, complicated equipment is needed for production and the problems have not been solved.

[Aim of invention]

The invention aims to provide a process for producing monolithic catalyst wherein noble metal is not impregnated in the peripheral zone in the monolithic support blocked by retainers.

[Constitution]

The inventors noted that a monolithic support is constituted as an assemblage of cells divided off by partitions such that, once it has entered a cell, gas or liquid is intercepted by the cell partitions and cannot permeate outward, and that noble metal is not impregnated to parts not coated with alumina. They realised that catalyst performance could be improved if the noble metal loading density per available unit volume was ultimately increased by applying the alumina coating treatment after the part closed by retainers had been masked off; and thus perfected the present invention.

Thus, the coating process and impregnation process for monolithic catalysts claimed for the invention is characterised comprising: a step wherein either the peripheral zone of one end of a monolithic support is coated over the desired width and alumina slurry is poured into the cells of the open central zone or a monolithic support the peripheral zone whereof is coated at both ends is immersed in alumina slurry, thereby depositing alumina slurry on the inner walls of the cells of the said central zone, and wherein the monolithic support is then dried and calcined to obtain a monolithic support comprising an alumina coated central zone and a non-alumina-coated peripheral zone; and a step wherein the said monolithic support clamped between upper and lower rings of the same diameter as the aforesaid central zone is immersed in an aqueous solution of noble metals or the said monolithic support with the peripheral zone of both ends coated is submerged and immersed in an aqueous solution of noble metals, and the support is then dried so that noble metals are impregnated only to the aforesaid central zone.

[Action and effect]

A monolithic support is normally a cordierite honeycomb substrate cut into a cylindrical form and has cells of rectangular or hexagonal cross-section and wall thickness about 0.3 mm running through the interior in the axial direction to form parallel channels at a density of around 300 cells/in<sup>2</sup>. Accordingly, if the monolithic support is mounted upright, the peripheral zone at the upper end is masked with the desired cladding material, and alumina slurry is poured into the open part, or if the peripheral zone at both ends is

masked and the support gently submerges in alumina slurry while held upright, alumina can in either case be coated on the unmasked central zone only. Impregnation with noble metals after alumina coating can be accomplished by the conventional method, and noble metals can thus be impregnated to the alumina-coated part only. However, while noble metals are difficult to impregnate to non-alumina-coated parts of the support, noble metal that simply deposits on the cell wall when the support is immersed in the aqueous solution of noble metals cannot function as a catalyst, effectively resulting in wastage of noble metals. To pre-empt this, therefore, it is desirable to prevent deposition of noble metal solution by some suitable means.

Working examples of the invention are hereunder described with reference to the drawings.

[Working examples]

#### *Working Example 1*

A monolithic support 1 of cordierite (diameter 100 mm × length 150 mm) is stood in the well of the upper lid of a settling tank 2 shown in Fig.1, and a receiving dish 3 in the bottom whereof a hole of diameter 90 mm has been made is mounted over the monolithic support 1. The size of the aforesaid hole has here been made equal to the diameter of the central zone 1a of the monolithic support 1 whereon noble metal is supported. Thus, the width  $X = 10$  mm of the peripheral zone 1b in the diagram is equal to the width of the retainer. Therefore, when coating slurry 5 of the composition shown hereunder is poured into the receiving dish 3 from the slurry pipe 4 while air is aspirated from the air extraction point 2a, the coating slurry 5 flows downward along the walls of the cells in the open central zone 1a, and after the prescribed amount of alumina has been deposited on the cell walls, the surplus slurry drops into the settling tank 2. The alumina coating slurry 5 consists of 100 parts by weight of commercial  $\gamma$ -alumina powder of mean specific surface area 100 m<sup>2</sup>/g, 70 parts by weight of alumina sol of alumina content 10 wt%, and 20 parts by weight of water.

The monolithic support so treated is dried in air and then calcined for 2 hours at 700°C, affording a monolithic support 1 wherein only the central zone 1a has been alumina coated, sparing the peripheral zone 1b blocked by the retainers. The central zone 1a and peripheral zone 1b can be freely defined by changing the receiving dish 3 to suit the width (X) of the retainers.

Although in principle the conventional method may be followed for impregnation with noble metals, impregnation is performed by the method set out below to avoid

unnecessary deposition of metals. Thus, a lower ring 7 of the same diameter as the central zone 1a is set in the middle of the tubular impregnation drum 6 shown in Fig.2 (a) and (b), the alumina-coated monolithic support 1 is mounted concentrically thereon, and an upper ring 8 of the same diameter as the lower ring 7 is superimposed. A rubber cuff 9 of thickness approximately 10 mm in a geometry that envelops the monolithic support 1 has been fitted in the impregnation drum 6 beforehand, so that when factory air is blown in from the air injection point 10, the rubber cuff 9 inflates; the monolithic support 1, the lower ring 7 and the upper ring 8 are thereby squeezed together and the monolithic support 1 can be held perpendicular. An aqueous dinitrodiammineplatinum solution (platinum 1.0 g/l) 11 is then poured into the centre of the upper ring 8 and the monolithic support 1 is completely saturated. After 60 min, air is extracted from the rubber cuff 9 and the monolithic support 1 is lifted out and dried for 1 hour at 200°C, providing a monolithic catalyst A of platinum loading density 1.56 g/l based on the volume of the central zone 1a.

#### *Working Example 2*

Tape 12 of width 10 mm equal to the width of the retainer is affixed at both ends to the peripheral zone of the same monolithic support 1 as in Working Example 1 and the said support is gently lowered into the impregnation drum 13 filled with coating slurry 5 whereupon the support sinks and is immersed therein as the air in the cells is expelled. After a prescribed time, the said support is extracted from the impregnation drum 13 and dried/calcined as in Working Example 1 to obtain a monolithic support 1 comprising an alumina-coated central zone 1a and a non-alumina-coated peripheral zone 1b in the same proportion as in Working Example 1.

The tape 12 is damaged in the calcination operation and is therefore stripped off; fresh tape 12 is affixed as before and the support is immersed in aqueous dinitrodiammineplatinum solution 11 of the same concentration as in Working Example 1 in another impregnation drum 13'. After 60 min, the monolithic support 1 is lifted out and dried for 1 hour at 200°C, affording a monolithic catalyst B of platinum loading density 1.56 g/l based on the volume of the central zone 1b [sic].

#### *Test example*

The monolithic catalysts A, B and C obtained in Working Examples 1 and 2 and by the prior art, respectively, were subjected to the following endurance test, after which an exhaust cleaning performance test was carried out. The endurance test consisted in measurement of percentage clean-up (%) for exhaust gas temperatures of 300°C and 350°C after operation for 300 hours at an air-fuel ratio (A/F) of 14.6, space velocity of

60,000 hr<sup>-1</sup> and catalyst intake gas temperature of 720°C. The results are presented in the table below.

Catalyst	Platinum loading density (g/l)	CO		NOx		HC	
		300°C	350°C	300°C	350°C	300°C	350°C
A	1.56	5	60	20	70	20	82
B	1.56	5	58	18	71	20	81
C	1.0	0	20	13	55	10	60

It will be clear from the aforesaid table that the monolithic catalysts A and B afforded by the invention have increased platinum loading per unit volume and an outstanding catalytic performance equal to or better than that of the monolithic catalyst C obtained by the conventional process.

The process of the invention thus enables the site of noble metal support in the monolithic catalyst to be freely defined by means of simple apparatus and operations, and since the noble metal is not impregnated in the part of the support blocked by retainers in the converter, the loading density per unit available volume increases and catalyst endurance is enhanced. Moreover, if the amounts of alumina and noble metal deposited or impregnated in the part blocked by retainer in the prior art are deducted in preparation of the alumina slurry and aqueous noble metal solution, economies in alumina and noble metal usage are achieved.

#### 4. Brief Description of Drawings

Fig.1 shows a sectional view of the alumina coating step in Working Example 1;

Fig.2 (a) shows a sectional view of the noble metal impregnation step in Working Example 1, and Fig.2 (b) shows a plan view of the impregnation drum;

Fig.3 (a) shows a sectional view of the alumina coating step in Working Example 2, and Fig.2 (b) shows a plan view of the impregnation drum;

Fig.4 (a) shows a sectional view of the noble metal impregnation step in Working Example 2, and Fig.2 (b) shows a plan view of the impregnation drum;

wherein

- |                            |                     |
|----------------------------|---------------------|
| 1... monolithic support,   | 1a... central zone  |
| 1b... peripheral zone      | 2... settling tank  |
| 2a... air extraction point | 3... receiving dish |
| 4... slurry pipe           |                     |

5... coating slurry

6... impregnation drum

8... upper ring

10... air injection point

11... aqueous dinitrodiammineplatinum solution

12... tape

7... lower ring

9... rubber cuff

13,13'...impregnation drum

Applicant: Toyota Motor Corp.

Agent: M.Hanabusa & Associate, Patent Attorneys

Fig.1

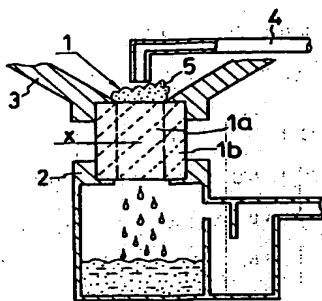


Fig.2

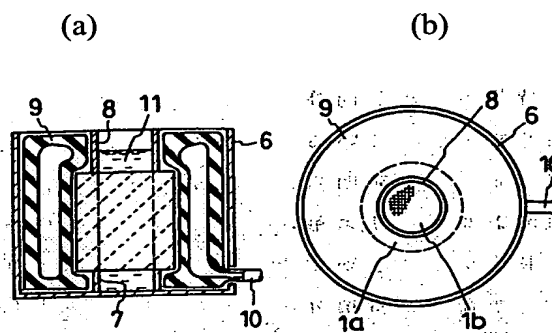


Fig.3

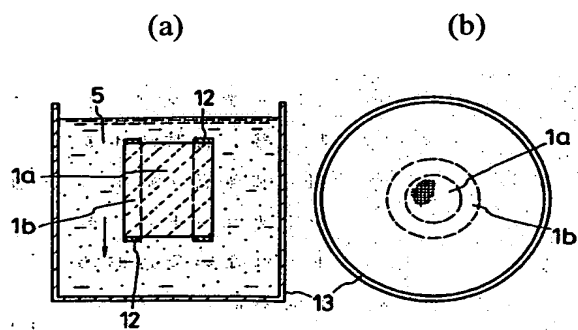


Fig.4

